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FUSER MEMBER OVERCOATED WITH
FLUOROCARBON-SILICONE RANDOM
COPOLYMER CONTAINING ALUMINUM
OXIDE

First Named Inventor (or Application Identifier):

Jiann H. Chen, et al

Enclosed are:

1. ☒ Specification
2. ☐ Sheet(s) of drawing(s)
3. ☒ Information Disclosure Statement Under 37 CFR 1.97.
4. Combined Declaration for Patent Application and Power of Attorney:
 - 4a. ☒ New
 - 4b. ☐ Copy from a prior application (37 CFR 1.63(d)) (for continuation/divisional with Box 11 completed)
5. ☐ Incorporation by Reference (useable if Box 4b is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.
6. ☒ Assignment of the invention to **NexPress Solutions LLC**
7. ☐ Certified copy of a priority
8. ☐ Associate Power of Attorney
9. ☐ Deletion of Inventor(s).
Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).

10. ☐ If a 111A application prior to examination of the above-identified application, amend the specification at Page 1, after the title, by inserting the following:
--CROSS REFERENCE TO RELATED APPLICATION
Reference is made to and priority claimed from U.S. Provisional Application Serial No. , filed , entitled .

If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

11. ☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No. ,
12. ☒ Please address all written communications to Lawrence P. Kessler,
c/o Eastman Kodak Company, 343 State Street, Rochester, NY 14650-2201.
Please Direct all telephone calls to Raymond L. Owens at (716) 477-4653.

The filing fee has been calculated as shown below:

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ORIGINAL PATENT APPLICATION BASED ON:

Docket: 80914RLO

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FUSER MEMBER OVERCOATED WITH FLUOROCARBON-SILICONE
RANDOM COPLOYMER CONTAINING ALUMINUM OXIDE

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FUSER MEMBER OVERCOATED WITH FLUOROCARBON-SILICONE
RANDOM COPOLYMER CONTAINING ALUMINUM OXIDE

CROSS REFERENCE TO RELATED APPLICATION

- Reference is made to commonly-assigned U.S. Patent Application
- 5 Serial No. _____, filed concurrently herewith, entitled "Fluorocarbon-Silicone Random Copolymer For Use in Toner Release Layer" by Chen et al, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

- This invention relates to fuser members useful for heat-fixing a
- 10 heat-softenable toner material to a substrate. More particularly, the invention relates to materials usable as a toner release layer in a fuser member.

BACKGROUND OF THE INVENTION

- Heat-softenable toners are widely used in imaging methods such as electrostatography, wherein electrically charged toner is deposited imagewise on a
- 15 dielectric or photoconductive element bearing an electrostatic latent image. Most often in such methods, the toner is then transferred to a surface of another substrate, such as, a receiver sheet comprising paper or a transparent film, where it is then fixed in place to yield the final desired toner image.

- When heat-softenable toners, comprising, thermoplastic polymeric
- 20 binders, are employed, the usual method of fixing the toner in place involves applying heat to the toner once it is on the receiver sheet surface to soften it and then allowing or causing the toner to cool.

- One such well-known fusing method comprises passing the toner-bearing receiver sheet through the nip formed by a pair of opposing rolls, at least
- 25 one of which (usually referred to as a fuser roll) is heated and contacts the toner-bearing surface of the receiver sheet in order to heat and soften the toner. The other roll (usually referred to as a pressure roll) serves to press the receiver sheet into contact with the fuser roll. In some other fusing methods, the configuration is varied and the "fuser roll" or "pressure roll" takes the form of a flat plate or belt.
- 30 The description herein, while generally directed to a generally cylindrical fuser roll in combination with a generally cylindrical pressure roll, is not limited to fusing

systems having members with those configurations. For that reason, the term “fuser member” is generally used herein in place of “fuser roll” and the term “pressure member” in place of “pressure roll.”

5 The fuser member usually comprises a rigid core covered with a resilient material, which will be referred to herein as a “base cushion layer.” The resilient base cushion layer and the amount of pressure exerted by the pressure member serve to establish the area of contact of the fuser member with the toner-bearing surface of the receiver sheet as it passes through the nip of the fuser member and pressure members. The size of this area of contact helps to establish
10 the length of time that any given portion of the toner image will be in contact with and heated by the fuser member. The degree of hardness (often referred to as “storage modulus”) and stability thereof, of the base cushion layer are important factors in establishing and maintaining the desired area of contact.

In some previous fusing systems, it has been advantageous to vary
15 the pressure exerted by the pressure member against the receiver sheet and fuser member. This variation in pressure can be provided, for example in a fusing system having a pressure roll and a fuser roll, by slightly modifying the shape of the pressure roll. The variance of pressure, in the form of a gradient of pressure that changes along the direction through the nip that is parallel to the axes of the
20 rolls, can be established, for example, by continuously varying the overall diameter of the pressure roll along the direction of its axis such that the diameter is smallest at the midpoint of the axis and largest at the ends of the axis, in order to give the pressure roll a sort of “bow tie” or “hourglass” shape. This will cause the pair of rolls to exert more pressure on the receiver sheet in the nip in the areas near
25 the ends of the rolls than in the area about the midpoint of the rolls. This gradient of pressure helps to prevent wrinkles and cockle in the receiver sheet as it passes through the nip. Over time, however, the fuser roll begins to permanently deform to conform to the shape of the pressure roll and the gradient of pressure is reduced or lost, along with its attendant benefits. It has been found that permanent
30 deformation (alternatively referred to as “creep”) of the base cushion layer of the fuser member is the greatest contributor to this problem.

Particulate inorganic fillers have been added to base cushion layers to improve mechanical strength and thermal conductivity. High thermal conductivity is advantageous when the fuser member is heated by an internal heater, so that the heat can be efficiently and quickly transmitted toward the outer surface of the fuser member and toward the toner on the receiver sheet it is intended to contact and fuse. High thermal conductivity is not so important when the roll is intended to be heated by an external heat source.

Optimal metal-particle filled elastomer fuser members have long been sought. At one time, it was predicted that:

“The metal of the metal-containing filler dispersed in the elastomer may be easily selected by one skilled in the art without undue experimentation by testing the metal-containing filler, such as a metal, metal alloy, metal oxide, metal salt or other metal compound, in an elastomer. The general classes of metals which are applicable to the present invention include those metals of Groups Ib, 2; 2b, 3; 3b, 4a, 4b, 5; 5b, 6b, 7b, 8 and the rare earth elements of the Periodic Table.” (U.S. Patent No. 4,264,181 to Lentz et al, column 10, lines 42-53; also U.S. Patent No. 4,272,179 to Seanor, column 10, lines 45-54.)

This prediction of easy selection of the metal for a metal-containing filler is not correct in view of subsequent work.

A metal-containing filler which provides good results in one elastomer may provide very poor results in another elastomer, even if the elastomers are very similar.

U.S. Patent No. 4,515,884 to Field et al, discloses a fuser member which utilizes metal oxide filled polydimethylsiloxane. The metal oxides are iron oxide and tabular alumina. Calcined alumina is described as being unsuitable per se. (column 9, line 50-column 10, line 47).

In U.S. Patent No. 4,264,181 to Lentz et al, good results were obtained when lead oxide was used as a filler in various fluorocarbon elastomers (Viton E430, Viton E605C, Viton GHTM; Examples X, XI, XII). In U.S. Patent

No. 5,017,432 to Eddy et al, on the other hand, teaches that oxide fluorocarbon elastomers (for example, Viton GFTM) would produce an unacceptable fuser member. In fluoroelastomers, cupric oxide is preferred.

U.S. Patent No. 4,272, 179 to Seanor and U.S. Patent Nos.

5 4,264,181 and 4,257,699 to Lentz teach the use, as a release oil, of a polydimethylsiloxane that incorporates mercapto functional groups. These patents indicate that lead oxide filler in the outer elastomer release layer interacts with the mercapto functionalized PDMS fluid to yield a release film on the surface of the fuser member.

10 Preparation of metal containing elastomers remains problematic. U.S. Patent No. 4,515,884 to Field et al, and U.S. Patent No. 5,017,432 to Eddy et al, cite large numbers of critical features or important aspects of their metal containing elastomers: choice of material (Field, column 9, lines 50-65 and column 10, lines 24-25), interaction of filler surface and elastomer (Field, column 9, lines 32-65), particle size (Field, column 10, lines 1-8 and lines 25-30; Eddy, 15 column 9, line 65—column 10, line 3), concentration of metal-filler (Field, column 10, lines 9-23 and lines 3 1-47), capability of interacting with functional groups of release agent (Eddy, column 9, lines 26-30), reactivity of the metal filler with the elastomer (Eddy, column 9, lines 3 3-43), and acid-base characteristics of 20 the metal filler (Eddy, column 9, lines 43-56). The lists of critical features and important aspects in Field and Eddy do not fully correlate. It is unknown whether this difference represents real differences in material characteristics or only differences in techniques and analysis.

In electrophotographic fuser systems, fuser members are commonly 25 made with an overcoat release layer of polysiloxane elastomer, polyfluorocarbon resin, or polyfluorocarbon elastomer.

Polysiloxane elastomers have relatively high surface energy and relatively low mechanical strength, but are adequately flexible and elastic and can produce high quality fused images. After a period of use, however, the self release 30 property of the roller degrades and offset begins to occur. Application of a

polysiloxane fluid during roller use enhances the ability of the roller to release toner, but shortens roller life due to oil absorption. Oiled portions tend to swell and wear and degrade faster.

One type of material that has been widely employed in the past to
5 form a resilient base cushion layer for fuser rolls is condensation-crosslinked siloxane elastomer. Disclosure of filled condensation-cured poly(dimethylsiloxane) "PDMS" elastomers for fuser rolls can be found, for example, in U.S. Patent Nos. 4,373,239; 4,430,406; and 4,518,655. U.S. Patent No. 4,970,098 to Ayala-Esquillin et al teaches a condensation cross-linked
10 diphenylsiloxane-dimethylsiloxane elastomer having 40 to 55 weight percent zinc oxide, 5 to 10 weight percent graphite, and 1 to 5 weight percent ceric dioxide.

A widely used siloxane elastomer is a condensation-crosslinked PDMS elastomer, which contains about 32-37 volume percent aluminum oxide filler and about 2-6 volume percent iron oxide filler, and is sold under the trade
15 name, EC4952, by the Emerson Cummings Co., U.S.A. It has been found that fuser rolls containing EC4952 cushion layers exhibit serious stability problems over time of use, i.e., significant degradation, creep, and changes in hardness, that greatly reduce their useful life. Mechanical Energy Resolver (MER) test results correlate with and thus accurately predict the instability exhibited during actual
20 use. Nevertheless, materials such as EC4952 initially provide very suitable resilience, hardness, and thermal conductivity for fuser roll cushion layers. See U.S. Patent No. 5,595,823.

U.S. Patent No. 5,582,917 discloses toner fusing members which have a substrate coated with a fluorocarbon-silicone polymeric composition.
25 Although these toner fusing members have proved effective they have a problem in that there can be toner contamination and may have a problem with low thermal conductivity. The advantage of using the fluorocarbon random copolymer containing aluminum oxide is that the aluminum oxide have been added to improve the thermal conductivity.

U.S. Patent No. 5,595,823 discloses toner fusing members which have a substrate coated with a fluorocarbon random copolymer containing aluminum oxide. Although these toner fusing members have proved effective and desirable thermal conductivity, they have a problem in that there can be toner contamination. The advantage of using the fluorocarbon silicone compositions is that they are effective for use with toner release agents which typically include silicone.

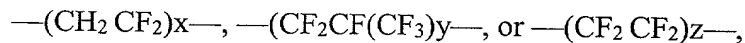
It would be desirable to provide a fuser member with an overcoat layer includes aluminum oxide filler and polyfunctional siloxane polymer to have a high thermal conductivity and low toner contamination.

SUMMARY OF THE INVENTION

It is an object of the invention to provide materials for forming a toner release layer.

It is another object of the present invention to provide a fuser member which makes use of fluorocarbon silicone but which has improved toner release and mechanical strength.

These objects are achieved by a fuser member comprising a core and a layer overlying the core, the layer including a fluorocarbon random copolymer, a curing agent which cures the fluorocarbon random copolymer, the cured fluorocarbon random copolymer having subunits of:



wherein

- x is from 30 to 90 mole percent,
- y is from 10 to 70 mole percent,
- z is from 0 to 34 mole percent;
- x + y + z equals 100 mole percent;

the layer further including a particulate filler having aluminum oxide and alkaline earth metal oxides or alkaline earth metal hydroxides or combinations thereof; and

a siloxane polymer comprising one or more curable, silanol-terminated, polyfunctional poly(C1-6 alkyl)siloxane polymers.

It is a feature of the present invention that a fuser member formed with a toner release layer that includes a metal oxide filled polyfluorocarbon elastomer has a moderate surface energy and that by using a fluorocarbon-silicone polymeric composition an improved fuser member is provided. Aluminum oxide
5 filler and siloxane polymer when added to the claimed combination provide improved thermal conductivity and reduce toner contamination.

A further advantage of the present invention is particular fillers such as inorganic base have been added to the fluorocarbon random copolymer in the presence of bisphenol curing agent to improve the mechanical strength.

10

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross sectional view of a fusing member in accordance with the present invention.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

FIG. 1 shows a cross sectional view of a fuser member 10 which
15 include a fuser roller, pressure roller, oiler donor roller, oiler metering roller, or pre-conditioning roller, etc. The core 16 is usually metallic, such as stainless steel, steel, aluminum, etc.; however, the core 16 may also be made of a ceramic or plastic. The primary requisites for core 16 materials are that it provide the necessary stiffness, be able to support the force placed upon it, and be able to
20 withstand whatever temperature to which it is subjected. Disposed above the core 16 lies one or more optional intermediate layers 14 which are characterized in the art as cushion layers. The outermost layer 12 is a toner release layer. In the event that a cushion layer 14 is desired, then the outermost layer 12 is disposed directly over the core 16. The outermost layer 12 is the toner release layer, it includes a
25 curing agent and a fluorocarbon random copolymer that is cured by the curing agent, the fluorocarbon random copolymer has subunits of:

- (CH₂ CF₂)_x— (vinylidene fluoride subunit (“VF₂”)),
- (CF₂CF(CF₃))_y— (hexafluoropropylene subunit (“HFP”)), and
- (CF₂ CF₂)_z—(tetrafluoroethylene subunit (“TFE”))

wherein

x is from 30 to 90 mole percent,

y is from 10 to 70 mole percent,

z is from 0 to 34 mole percent; and

5 x + y + z equals 100 mole percent;

the layer further including particulate filler having aluminum oxide;

and

a siloxane polymer comprising one or more curable, silanol-terminated, polyfunctional poly(C1-6 alkyl)siloxane polymers.

10 It is a feature of the present invention that a fuser member formed with a toner release layer that includes a metal oxide filled polyfluorocarbon elastomer has a moderate surface energy and that by using a fluorocarbon-silicone polymeric composition an improved fuser member is provided. Aluminum oxide filler and siloxane polymer when added to the claimed combination provide
15 improved thermal conductivity and reduce toner contamination.

In these formulas, x, y, and z are mole percentages of the individual subunits relative to a total of the three subunits (x+y+z), referred to herein as “subunit mole percentages” (The curing agent can be considered to provide an additional “cure-site subunit”, however, the contribution of these cure-site
20 subunits is not considered in subunit mole percentages.) In the fluorocarbon copolymer, x has a subunit mole percentage of from 30 to 90 mole percent, y has a subunit mole percentage of from 10 to 70 mole percent, and z has a subunit mole percentage of from 0 to 34 mole percent. In a currently preferred embodiment of the invention, subunit mole percentages are: x is from 40 to 80, y is from 10 to 60,
25 and z is from 0 to 34; or more preferably x is from 42 to 75, y is from 14 to 58, and z is 0. In the currently preferred embodiments of the invention, x, y, and z are selected such that fluorine atoms represent at least 70 percent of the total formula weight of the VF₂, HFP, and TFE subunits.

Preferably, curable polyfunctional poly(C1-6 alkyl)siloxane
30 polymers are also used in the present invention and are cured concurrently with the fluorocarbon random copolymer when cured by the curing agent to produce a

coating suitable for use as the toner release layer of a fusing member. In accordance with the invention, coated fusing members have low energy surfaces which release toner images with minimal offset. These coatings can also be advantageously used with small amounts of externally added polymeric release

5 agents, for example mercapto functionalized polydimethylsiloxanes, to further minimize offset. Preferred curable polyfunctional poly(C1-6 alkyl)siloxane polymers are heat-curable silicones, however peroxide-curable silicones can also be used with conventional initiators. Heat-curable silicones include the hydroxy-functionalized polyfunctional organopolysiloxanes belonging to the class of
10 silicones known as "soft" silicones. Preferred soft silicones are silanol-terminated polyfunctional organopolysiloxanes containing repeating units of the formula,



wherein R1 is C1-6 alkyl and a is 0 to 3. Alkyl groups which R1 can represent include methyl, ethyl, propyl, isopropyl, butyl, sec. butyl, pentyl and hexyl.

15 Preferred soft silicones are those in which R1 is methyl. The soft silicones can be used singly or as mixtures of silicones and can contain various proportions of mono-, di-, tri- and tetra-functional siloxane repeating units. Preferred soft silicones comprise a major component of a silanol- or trimethylsilyl-terminated polydimethylsiloxane having a number average molecular weight between about
20 20,000 to 300,000 and a minor component of a polymethylsiloxane comprising monofunctional and tetrafunctional siloxane repeating units and having a number average molecular weight in the range of 1,000 to 10,000. Exemplary soft silicones are commercially available or can be prepared by conventional methods, for example, SFR-100 silicone (sold by General Electric Co.) and EC 4952
25 silicone (sold by Emerson Cummings Co.). SFR-100 silicone is characterized as a silanol- or trimethylsilyl-terminated polymethylsiloxane and is a liquid blend comprising about 60-80 weight percent of a difunctional polydimethylsiloxane having a number average molecular weight of about 150,000, and 20-40 weight percent of a polytrimethylsilyl silicate resin having monofunctional (i.e.
30 trimethylsiloxane) and tetrafunctional (i.e. SiO₂) repeating units in an average

ratio of between about 0.8 and 1 to 1 and having a number average molecular weight of about 2,200. EC 4952 silicone is characterized as a silanol-terminated polymethylsiloxane having about 85 mole percent of difunctional dimethylsiloxane repeating units, about 15 mole percent of trifunctional

5 methylsiloxane repeating units and having a number average molecular weight of about 21,000. Other polyfunctional poly(C1-6 alkyl)siloxane polymers which can be used are disclosed in U.S. Patent Nos. 4,387,176 and 4,536, 529, the disclosures of which are hereby incorporated by reference.

In one aspect of the invention a fluorocarbon-silicone composite is
10 obtained which can be used as a fusing roll layer without adding release agents and with- out causing offset. Suitable fluorocarbon random copolymers are the terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluorethylene having a fluorine content of at least about 70 mole percent as disclosed in U.S. Patent No. 5,035,950. The silicone component of the composite is a soft silicone,
15 for example, a polymethylsiloxane com-position such as SFR-100 silicone.

Preferred composites of the invention have a ratio of siloxane polymer to fluorocarbon copolymer between about 0.1 and 3 to 1 by weight, preferably between about 0.2 and 0.5 to 1. The composite is preferably obtained by curing a mixture comprising from about 50-70 weight percent of a
20 fluorocarbon copolymer, 10-30 weight percent of a curable polyfunctional polymethylsiloxane polymer, most preferably about 20-30 weight percent. 1-10 weight percent of a fluorocarbon-curing agent, 1-3 weight percent of a fluorocarbon-curing accelerator, 8-30 weight percent of an acid acceptor type filler, and 10-30 weight percent of an inert filler.

25 Curing of the composite is carried out according to the well known conditions for curing vinylidene fluoride based copolymers ranging, for example, from about 12- 48 hours at temperatures of between 50°C. to 250°C. Preferably the coated composition is dried until solvent free at room temperature, then gradually heated to about 230 °C. over 24 hours, then maintained at that
30 temperature for 24 hours.

The outer layer includes particulate filler comprising aluminum oxide and additional particulate selected from alkaline earth metal oxides, alkaline earth metal hydroxides, and combinations of alkaline earth metal oxides and hydroxides. In a currently preferred embodiment of the invention, the additional
5 particulate is a mixture of magnesium oxide and calcium hydroxide. The particulate filler has a total concentration in the outer layer of from about 13 to 170 parts per hundred parts by weight of the fluorocarbon random copolymer (pph). The aluminum oxide has a concentration of from about 10 to 140 parts per hundred parts (pph) by weight of the fluorocarbon random copolymer.
10 Concentrations of aluminum oxide of less than 10 parts by weight may not provide the degree of stability desired to the layer. Concentrations of aluminum oxide of greater than 140 parts by weight will render the layer too hard to provide the desired area of contact with the toner-bearing receiver sheet. In a particular embodiment of the invention, the outer layer has 3 pph of MgO, 6 pph of
15 Ca(OH)_2 and from 10 to 140 pph of aluminum oxide.

The aluminum oxide particles employed as filler in the base cushion layer of a fuser member of the invention can be obtained from any convenient commercial source, e.g., Magnesium Electron, Inc. of Flemington, N.J. The particle size does not appear to be critical. Particle sizes anywhere in the range of
20 0.1 to 100 micrometers have been found to be acceptable. In the examples presented below the aluminum oxide particles were from 1 to 40 micrometers in diameter.

To form the outer layer, the filler particles are mixed with the uncured polymer, crosslinking agent, and any other additives, such as an
25 accelerator; shaped over the base cushion, and cured. The fluorocarbon is cured by crosslinking with basic nucleophile addition curing. Basic nucleophilic cure systems are well known and are discussed, for example, in U.S. Patent No. 4,272,179. One example of such a cure system combines a bisphenol as the crosslinking agent and an organophosphonium salt, as an accelerator.

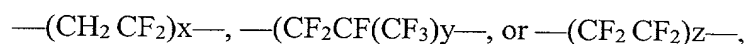
The crosslinker is incorporated into the polymer as a cure-site subunit, for example, bisphenolic residues. Other examples of nucleophilic addition cure systems are sold commercially as DIAK No. 1 (hexamethylenediamine carbamate) and DIAK No. 3 (N,N'-dicinnamylidene-1,6-hexanediamine) by E.I. duPont de Nemours & Co.

Suitable uncured polymers are available commercially. In a particular embodiment of the invention, a vinylidene fluoride-co-hexafluoropropylene was used which can be represented as $-(VF)(75)-(HFP)(25)-$. This material is marketed by E.I. duPont de Nemours and Company under the designation "Viton A" and is referred to herein as "Viton A". In another embodiment of the invention, a vinylidene fluoride-co-hexafluoropropylene was used which can be represented as $-(VF)(42)-(HFP)(58)-$. This material is marketed by Minnesota Mining and Manufacturing, St. Paul, Minn, under the designation "Fluorel FX-2530" and is referred to herein as "FX-2S30". Other suitable uncured vinylidene fluoride-cohexafluoropropylenes and vinylidene fluoride-co-tetrafluoroethylene-cohexafluoropropylenes are available, for example, Fluorel FX-9038.

The molecular weight of the uncured polymer is largely a matter of convenience, however, an excessively large or excessively small molecular weight would create problems, the nature of which are well known to those skilled in the art. In a preferred embodiment of the invention the uncured polymer has a number average molecular weight in the range of about 100,000 to 200,000.

The fuser member is constructed forming a toner release layer on a overlying an optional base cushion provided on a core comprising the steps of:

- (a) providing a core;
 - (b) providing a mixture having:
 - (i) a fluorocarbon random copolymer having subunits
- of:



wherein

x is from 30 to 90 mole percent,

y is from 10 to 70 mole percent,

z is from 0 to 34 mole percent;

5 x + y + z equals 100 mole percent;

(ii) a particular fillers comprising aluminum oxide and additional particulate selected from alkali metal oxides, alkali metal hydroxides, and combinations of alkali metal oxides and hydroxides; and

(iii) a crosslinking agent and a crosslinking accelerator;
10 and a siloxane polymer comprising one or more curable, silanol-terminated, polyfunctional poly(C1-6 alkyl)siloxane polymers, the siloxane polymer comprising at least two different functional siloxane units selected from the group consisting of monofunctional, difunctional, trifunctional and tetrafunctional siloxane units, and creating an interpenetrating network consisting essentially of
15 separately crosslinked polymers, the fluorocarbon random copolymer and the fluorocarbon curing agent forming one crosslinked polymer, and the siloxane polymer forming a second crosslinked polymer; and

(c) applying the mixture to the base cushion and curing the applied mixture to crosslink the fluorocarbon random copolymer.

20 In cases where it is intended that the fuser member be heated by an internal heater, it is desirable that the outer layer have a relatively high thermal conductivity, so that the heat can be efficiently and quickly transmitted toward the outer surface of the fuser member that will contact the toner intended to be fused. (Depending upon relative thickness, it is generally even more desirable that the
25 base cushion layer and any other intervening layers have a relatively high thermal conductivity. Suitable materials for the base cushion layer are discussed below).

Some fusing systems use a release oil, such as a PDMS oil, to prevent offset, that is, to aid the roll in releasing from the toner it contacts during the fusing operation. During use, the oil is continuously coated over the surface of
30 the fuser member in contact with the toner image. The fuser member of the invention can be used with polydimethylsiloxane, amino functionalized

polydimethylsiloxane or mercapto functionalized polydimethylsiloxane release oils at normally used application rates or at reduced application rates, from about 0.5 mg/copy to 10 mg/copy (the copy is 8.5 by 11 inch 20 pound bond paper.)

The outer layer of the fuser member of the invention is
5 substantially resistant to release oil induced swelling. In a preferred embodiment of the invention, the change in size due to swelling is less than 0.1 to 1.0 percent. In an even more preferred embodiment of the invention, the change in size due to swelling is less than 0.01 to 0.1 percent.

The thickness of the base cushion and outer layers and the
10 composition of the base cushion layer can be chosen so that the base cushion layer can provide the desired resilience to the fuser member, and the outer layer can flex to conform to that resilience. The thickness of the base cushion and outer layers will be chosen with consideration of the requirements of the particular application intended. Usually, the outer layer would be thinner than the base cushion layer.
15 For example, base cushion layer thickness in the range from 0.6 to 5.0 mm have been found to be appropriate for various applications. In some embodiments of the present invention, the base cushion layer is about 2.5 mm thick, and the outer layer is from about 25 to 30 mm thick.

Suitable materials for the base cushion layer include any of a wide
20 variety of materials previously used for base cushion layers, such as the condensation cured polydimethylsiloxane marketed as EC4952 by Emerson Curning. An example of a condensation cured silicon rubber base cushion layer is GE 4044 marketed by General Electric of Waterford, N.Y. An example of an addition cured silicone rubber is Silastic J RTV marketed by Dow Corning applied
25 over a silane primer DC-1200 also marketed by Dow Corning.

In a particular embodiment of the invention, the base cushion is
resistant to cyclic stress induced deformation and hardening. Such materials when subjected to cyclic stress using an MER, as above discussed, exhibit changes in length and hardness (storage modulus) of less than about 20 percent. Examples of
30 suitable materials are filled condensation-crosslinked PDMS elastomers disclosed in U.S. Patent No. 5,269,740 (copper oxide filler), U.S. Patent No. 5,292,606 (zinc

oxide filler), U.S. Patent No. 5,292,562 (chromium oxide filler), U.S. Patent No. 5,480,724 (tin oxide filler), U.S. Patent No. 5,336,539 (nickel oxide filler). These materials all show reasonable heat conductivities and much less change in hardness and creep than EC4952 or the PDMS elastomer with aluminum oxide
5 filler. Additional suitable base cushions are disclosed in U.S. Patent Nos. 5,466,533, 5,474,852; and 5,464,703, the disclosures of which are hereby incorporated herein by reference.

The core of the fuser member is usually cylindrical in shape. It comprises any rigid metal or plastic substance. Metals are preferred when the
10 fuser member is to be internally heated, because of their generally higher thermal conductivity. Suitable core materials include, e.g., aluminum, steel, various alloys, and polymeric materials such as thermoset resins, with or without fiber reinforcement. The core can be a support which has been conversion coated and primed with metal alkoxide primer in accordance with U.S. Patent No. 5,474,821,
15 which is hereby incorporated by reference.

The fuser member is mainly described herein in terms of embodiments in which the fuser member is a fuser roll having a core, a base cushion layer overlying the core, and an outer layer superimposed on the base cushion. The invention is not, however, limited to a roll, nor is the invention
20 limited to a fusing member having a core bearing two layers: the base cushion layer and the outer layer. The fuser member of the invention can have a variety of outer configurations and layer arrangements known to those skilled in the art. For example, the base cushion layer could be eliminated or the outer layer described herein could be overlaid by one or more additional layers.

25 The invention is further illustrated by the following Examples and Comparative Examples.

EXAMPLES 1-3

A cylindrical stainless steel core was cleaned with dichloromethane and dried. The core was then primed with a uniform coat of a metal alkoxide type
30 primer, Dow 1200 RTV Prime Coat primer, marketed by Dow Corning Corporation of Midland, Mich.; which contains: light aliphatic petroleum naptha

(85 weight percent), tetra (2-methoxyethoxy)-silane (5 weight percent), tetrapropyl orthosilicate (5 weight percent), and tetrabutyl titanate (5 weight percent). Silastic.RTM. J RTV room temperature vulcanizing silicone rubber, marketed by Dow Corning Corporation of Midland, Mich.; was then mixed with catalyst and injection molded onto the core and cured at 232°C. for 2 hours under 75 tons/inch² of pressure. The roller was then removed from the mold and baked in a convection oven with a temperature ramp increasing to 23°C. substantially uniformly over 24 hours and then maintaining that temperature for an additional 24 hours. After air cooling, EC4952 marketed by Emerson Cumming Division of W. R. Grace and Co. of Connecticut was blade coated directly onto the Silastic J layer, then cured for 12 hours at about 210°C., followed by 48 hours at 218°C. in a convection oven. After air cooling, the EC4952 was ground to a thickness of 20 mils. The cured EC4952 was corona discharged for 15 minutes at 750 watts and an outer layer was applied.

Fluorocarbon random copolymer and soft silicone SFR-100 was mixed as indicated in Table 1 with varying amounts of aluminum oxide. Viton A is a commercially available fluorocarbon random copolymer which is sold by duPont Corporation. Column 2 sets forth the parts per hundred (pph) of a fluorocarbon random copolymer. The weight fraction of fluorocarbon random copolymer and soft silicone SFR-100 was held constant. Each of the formulations was mixed with 2.5g of Viton Curative 20 and 6g of Viton curative 30 (products made by the duPont Corporation). The formulations were all mixed on a two-roll mill then dissolved to form a 25 weight percent solids solution in methyl ethyl ketone. Part of the resulting material was ring coated onto the cured EC4952 layer, air dried for 16 hours, baked with 24 hour ramp to 260°C. and then a 24 hour soak at 260°C. The Silastic J layer had a thickness of 380 mils. The resulting outer layer of fluorocarbon random copolymer had a thickness of 1 mil. The remainder of the material was cast to a film and allowed to dry for 3 days. Afterwards the cast films were baked with 24 hour ramp to 260°C. and then a 24 hour soak at 260°C.

Table 1

	Viton A	pph / SFR-100	pph / Al ₂ O ₃
E1	100	20	10
E2	100	20	50
E3	100	20	140

COMPARATIVE EXAMPLES 1-5

Substantially the same procedures were followed as in Examples 1-3, except that in lieu either of SFR-100 or aluminum oxide or none of both was added as indicated in Table 2.

Table 2

	Viton A	pph / SFR-100	pph / Al ₂ O ₃
C1	100	20	0
C2	100	0	0
C3	100	0	10
C4	100	0	50
C5	100	0	140

Materials Testing

Thermal conductivity of thin film is measured by Thermal Conductivity Analyzer TCA-100 (HOLOMETRIX) by the guarded heat flow meter method in accordance with ASTM F433-77. Results are shown in Table 3.

Table 3

<u>Sample</u>	<u>pph / Al₂O₃</u>	<u>K</u>
E1	10	0.0828
E2	50	0.1406
E3	140	0.1962
C1	0	0.0837
C2	0	0.0837
C3	10	0.1061
C4	50	0.2043
C5	140	0.2758

Table 3 shows that the presence of the aluminum oxide increases the thermal conductivity both of the fluorocarbon- silicone random copolymer and the fluorocarbon random copolymer.

5

Toner Release Test

The test samples are employed to evaluate the toner offset and release force characteristics of the fuser member coating. Two samples are cut approximately 1-inch square of each example. One of these squares is left untreated by release agent (the dry sample). To the surface of the other sample is applied in unmeasured amount of Xerox amino-functionalized PDMS 8R79.

10

Each sample is incubated overnight at a temperature of 175°C. Following this treatment, the surface of each sample is wiped with dichloromethane. Each sample is then soaked in dichloromethane for one hour and allowed to dry before off-line testing for toner offset and release properties.

15

Each sample is tested in the following manner:

A one-inch square of paper covered with unfused polyester toner is placed in contact with a sample on a bed heated to 175°C, and a pressure roller set for 80 psi is locked in place over the laminate to form a nip. After 20 minutes the roller is released from the laminate.

The extent of offset for each sample is determined by microscopic examination of the sample surface following delamination. The following numerical evaluation, corresponding to the amount of toner remaining on the surface, is employed.

1	0% offset
2	1-20% offset
3	21-50% offset
4	51-90% offset
5	91-100% offset

- 5 Qualitative assessment of the force required for delamination of the from the samples is as follows:

1	low release force
2	moderate release force
3	high release force

Results are shown in Table 4.

Table 4

Sample	Dry Offset	Dry Release	Amino Offset	Amino Release
E1	0.6	2	0.2	1
E2	2	2	1	1
E3	1	2	0.2	1
C3	0.3	2	0.2	1
C4	3	2	1.5	1
C5	3	2	0.2	1

- 10 Table 4 shows a comparison between the fluorocarbon- silicone random copolymer and the fluorocarbon random copolymer when the aluminum oxide was added into both of the polymers. In terms of the toner release and offset, the fluorocarbon-silicone random copolymer shows the significantly improvement in the dry toner release and amino offset.

- 15 The above data and description show that the combination of aluminum oxide in conjunction with the fluorocarbon- silicone random copolymer

shows significant improvement of attainable properties. The positive attributes such as the increased thermal conductivity are maximized while negative attributes such as propensity to offset, lack of release are minimized. Aluminum oxide filler and siloxane polymer when added to the claimed combination provide
5 improved thermal conductivity and reduce toner contamination.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it should be appreciated that variations and modifications can be effected within the scope of the invention.

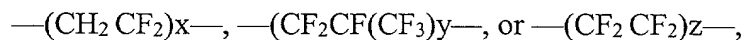
PARTS LIST

- 10 fuser member
- 12 outermost layer
- 14 intermediate layer
- 16 core

10 fuser member
12 outermost layer
14 intermediate layer
16 core

WHAT IS CLAIMED IS:

1. A fuser member comprising a core and a layer overlying the core, the layer including a fluorocarbon random copolymer, a curing agent which cures the fluorocarbon random copolymer, the cured fluorocarbon random copolymer having subunits of:



wherein

x is from 30 to 90 mole percent,

y is from 10 to 70 mole percent,

z is from 0 to 34 mole percent;

x + y + z equals 100 mole percent;

the layer further including a particulate filler having aluminum oxide and alkaline earth metal oxides or alkaline earth metal hydroxides or combinations thereof; and

a siloxane polymer comprising one or more curable, silanol-terminated, polyfunctional poly(C1-6 alkyl)siloxane polymers.

2. The fusing member of claim 1 wherein the siloxane polymer comprises at least two different functional siloxane units selected from the group consisting of monofunctional, difunctional, trifunctional and tetrafunctional siloxane units, and creating an interpenetrating network to cure the fluorocarbon random copolymer forming separately crosslinked polymers, the fluorocarbon random copolymer and the fluorocarbon curing agent forming one crosslinked polymer, and the siloxane polymer forming a second crosslinked polymer.

3. The fuser member of claim 1 wherein the aluminum oxide has a total concentration in the layer of from 10 to 140 parts by weight per 100 parts of the fluorocarbon random copolymer.

4. The fuser member of claim 2 wherein the alkaline earth metal oxides or alkaline earth metal hydroxides or combinations thereof have a total concentration in the layer of from 3 to 15 parts by weight per 100 parts of the fluorocarbon random copolymer.

5. The fuser member of claim 4 wherein the alkaline earth metal hydroxide includes calcium hydroxide and the alkaline earth metal oxide includes magnesium oxide.

6. The fuser member of claim 2 wherein the fluorocarbon random copolymer is crosslinked by bisphenolic residues.

7. The fuser member of claim 1 further including a cushion layer on the core.

8. The fuser member of claim 1 wherein the fluorocarbon random copolymer is nucleophilic addition cured.

9. The fuser member of claim 1 wherein x is from 40 to 80 mole percent, y is from 10 to 60 mole percent, and z is from 0 to 34 mole percent.

10. The fuser member of claim 1 wherein x is from 42 to 75 mole percent and y is from 14 to 58 mole percent,.

11. The fuser member of claim 1 wherein x is greater than 40 mole percent.

12. The fuser member of claim 1 wherein the curable polyfunctional poly(C1-6 alkyl)siloxane polymer is a heat-curable polymer.

13. The fuser member of claim 2 wherein the siloxane polymer includes a polydimethylsiloxane having a number average molecular weight of between about 20,000 to 300,000 and a polymethylsiloxane comprising monofunctional and tetrafunctional siloxane repeating units and having a number average molecular weight in the range of 1,000 to 10,000.

14. The fuser member of claim 1 wherein the siloxane polymer comprises a silanol- or trimethylsilyl-terminated polymethylsiloxane and is a liquid blend comprising about 60-80 weight percent of a difunctional polydimethylsiloxane having a number average molecular weight of about 150,000, and 20-40 weight percent of a polytrimethylsilyl silicate resin having monofunctional and tetrafunctional repeating units in an average ratio of between about 0.8 and 1 to 1, and having a number average molecular weight of about 2,200.

ABSTRACT OF THE DISCLOSURE

A fuser member comprising a core and a layer overlying the core, the layer including a fluorocarbon random copolymer, a curing agent which cures the fluorocarbon random copolymer, the cured fluorocarbon random copolymer
5 having subunits of:



wherein

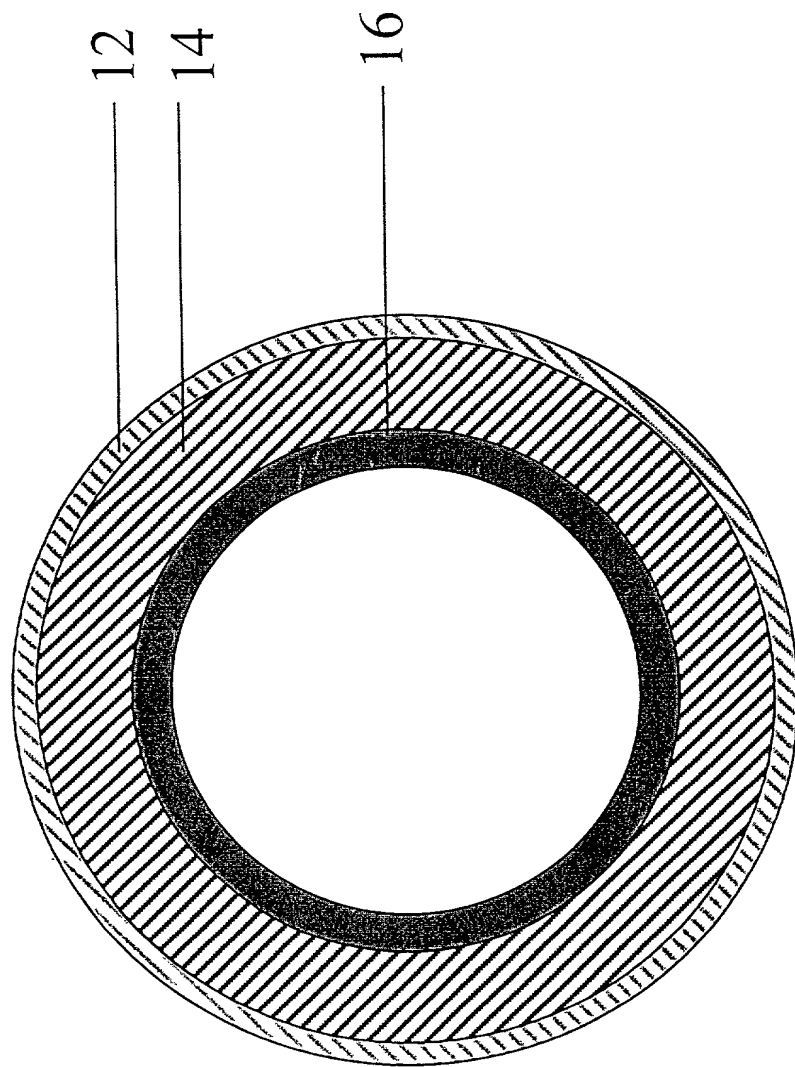
x is from 30 to 90 mole percent,

y is from 10 to 70 mole percent,

10 z is from 0 to 34 mole percent;

x + y + z equals 100 mole percent;

The layer further including a particulate filler having aluminum oxide and alkaline earth metal oxides or alkaline earth metal hydroxides or combinations thereof; and siloxane polymer comprising one or more curable,
15 silanol-terminated, polyfunctional poly(C1-6 alkyl)siloxane polymers.



10

Fig. 1

Combined Declaration For Patent Application and Power of Attorney

ATTORNEY DOCKET
80914RLO

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

FUSER MEMBER OVERCOATED WITH FLUOROCARBON-SILICONE RANDOM COPOLYMER CONTAINING ALUMINUM OXIDE

The specification of which (check only one item below):

☒ is attached hereto.☐ was filed as United States Application Serial No. on and
was amended on (if applicable).☐ was filed as PCT international application Number on and was amended under PCT Article 19 on (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the U.S. Patent & Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1 56

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign applications(s) for patent or inventor's certificate or any PCT international application(s) designating a least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT, indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC §119			
			<input type="checkbox"/>	YES	<input type="checkbox"/>	NO
			<input type="checkbox"/>	YES	<input type="checkbox"/>	NO
			<input type="checkbox"/>	YES	<input type="checkbox"/>	NO

I hereby claim the benefit under Title 35, United States Code, 119 §(e) of any United States provisional application(s) listed below:

PRIOR PROVISIONAL APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119 (e):

PROVISIONAL APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under Title 35, United States Code, §120 of any prior United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior applications(s) in the manner provided by the first paragraph of Title 35, §112, I acknowledge the duty to disclose to the U.S. Patent & Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations §1 56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR US APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S FOR BENEFIT UNDER 35USC§120:

U S APPLICATIONS			STATUS (Check one)		
U S APPLICATION NUMBER	U S FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U S					
PCT APPLICATION NO	PCT FILING DATE	U S SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (*List name and registration number*)

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6	BUSINESS ADDRESS	BUSINESS ADDRESS	CITY	STATE & ZIP CODE (COUNTRY)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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